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| (54) Title: ORGANIC ELECTROLUMINESCENT DEVICES WITH IMPROVED STABILITY IN AIR | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| (57) Abstract | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p>An electroluminescent device comprising at least one organic film, at least one of which is an electroluminescent organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes and electrons are injected into the electroluminescent organic film, resulting in light emission therefrom, wherein the cathode material comprises a film of ytterbium, or a metal film prepared by vapor deposition or sputtering of an alloy of magnesium and a second metal having a higher work function, such alloy having a magnesium content of from 80 to 98 percent.</p> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p style="text-align: center;">Luminance Comparison: Yb vs Ca Cathodes</p> <table border="1"> <caption>Approximate data points from the graph</caption> <thead> <tr> <th>Volts</th> <th>Cd/m², Ca</th> <th>Cd/m², Yb</th> </tr> </thead> <tbody> <tr> <td>3.5</td> <td>10</td> <td>15</td> </tr> <tr> <td>4.5</td> <td>100</td> <td>200</td> </tr> <tr> <td>5.5</td> <td>500</td> <td>800</td> </tr> <tr> <td>6.5</td> <td>1500</td> <td>2500</td> </tr> <tr> <td>7.5</td> <td>4000</td> <td>6000</td> </tr> <tr> <td>8.5</td> <td>8000</td> <td>12000</td> </tr> <tr> <td>9.5</td> <td>15000</td> <td>25000</td> </tr> <tr> <td>10.5</td> <td>30000</td> <td>50000</td> </tr> <tr> <td>11.5</td> <td>60000</td> <td>100000</td> </tr> </tbody> </table> | | | | Volts | Cd/m², Ca | Cd/m², Yb | 3.5 | 10 | 15 | 4.5 | 100 | 200 | 5.5 | 500 | 800 | 6.5 | 1500 | 2500 | 7.5 | 4000 | 6000 | 8.5 | 8000 | 12000 | 9.5 | 15000 | 25000 | 10.5 | 30000 | 50000 | 11.5 | 60000 | 100000 |
| Volts | Cd/m², Ca | Cd/m², Yb | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.5 | 10 | 15 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4.5 | 100 | 200 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5.5 | 500 | 800 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6.5 | 1500 | 2500 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 7.5 | 4000 | 6000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 8.5 | 8000 | 12000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 9.5 | 15000 | 25000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 10.5 | 30000 | 50000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 11.5 | 60000 | 100000 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

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ORGANIC ELECTROLUMINESCENT DEVICES WITH IMPROVED STABILITY IN AIR

This invention relates to electroluminescent devices, particularly those that contain films of organic material.

5 Organic film-containing electroluminescent (EL) devices typically consist of an organic film sandwiched between an anode material layer and a cathode material layer such that when a positive bias is applied to the device, holes are injected into the organic film from the anode and electrons are injected into the organic film from the cathode. The combination of a hole and an electron gives rise to an exciton which undergoes radiative
10 decay to the ground state by liberating a photon. The cathode is commonly a metallic film deposited on the surface of the organic film by either evaporation or sputtering.

 Since exciton formation results from the combination of a hole and an electron, balanced injection of both carriers is the key to device efficiency. Hole injection from indium-tin oxide (ITO) anodes is usually a facile process as its work function is close to
15 the ionization potentials of most organic materials. Electron injection is much more difficult to achieve, owing to the low electron affinity of most organic materials, and requires the use of more reactive, low work function metals. For example, Gao et. al. in Applied Physics Letters (Vol. 73, pp. 7894-7899 (1993)) reported the efficiency of poly(phenylenevinylene)-based devices can be improved by more than 100 times by using calcium (work function 2.5
20 to 3.0 electron volts (eV)) as the cathode instead of aluminum (work function 4.0 to 4.5 eV). However, the cathodes of these more efficient devices are less environmentally stable, since low work function metals are known to be extremely sensitive to oxygen and moisture in air. Indeed, devices with calcium cathodes have been reported to lose 90 percent of their efficiency in 37 seconds in highly humid environments (Sheats et. al. in Science, Vol. 273,
25 pp. 884-888 (1996)).

 Magnesium (work function 3.5 to 4.0 eV) is sometimes seen as a compromise cathode material as it is commonly accepted to be an air-stable metal. Yet, its durability in EL devices still leaves much to be desired as Tang and VanSlyke (U.S. Patent 4,885,211) had shown that efficiency of devices with magnesium cathodes may drop by more than an
30 order of magnitude in a matter of hours when exposed to ambient conditions with a relative humidity of 20 percent or higher, presumably due to fast corrosion. Tang and VanSlyke disclosed in U.S. Patent 4,885,211 magnesium-based cathodes formed by a co-deposition

process wherein magnesium and a second metal are evaporated from separate sources at different rates such that the atomic ratio of magnesium to the second metal is in the range of 99:1 to 90:10 in the resulting cathode. Preferred second metals are silver, indium and aluminum. Cathodes thus formed are smooth and adhere well to organic substrates.

- 5 However, the co-deposition process, although producing improved cathodes, is cumbersome as a manufacturing process since it requires that metals be evaporated from separate boats concurrently at precisely and individually controlled rates to provide the desired ratio of magnesium to second metal.

Accordingly, a relatively stable cathode material having a low work function
10 which is relatively easy to prepare would be highly desirable.

In one aspect, this invention is an electroluminescent device comprising at least one organic film, at least one of which is an electroluminescent organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes and electrons are injected into the electroluminescent
15 organic film, resulting in light emission therefrom;

wherein the cathode material comprises a film of ytterbium.

In a second aspect, this invention is an electroluminescent device comprising at least one organic film, at least one of which is an electroluminescent organic film, arranged between an anode material and a cathode material such that under an applied
20 voltage, the device is forward biased and holes and electrons are injected into the electroluminescent organic film, resulting in light emission therefrom;

wherein the cathode material comprises a metal film prepared by vapor deposition or sputtering of an alloy of magnesium and a second metal having a higher work function, such alloy having a magnesium content of from 80 to 98 percent.

25 It has been discovered that devices having an ytterbium cathode may be prepared which are not only relatively efficient, but surprisingly suffer little degradation in efficiency and brightness at a given voltage after having been exposed to ambient conditions for relatively long periods of time. It has also been discovered that EL devices with cathodes made by evaporation and vapor deposition of magnesium alloys are relatively simple to
30 prepare, yet have good adhesion and resistance to degradation in efficiency after having

been exposed to ambient conditions for relatively long periods of time. These and other advantages of the invention will be apparent from the description which follows.

Figures 1 and 2 illustrate the luminance and efficiency, respectively, of LED devices prepared using an Yb or Ca cathode, prepared as described in Example 1. Figures 3 and 4 illustrate the luminance of LED devices prepared using a Dowmetal or Mg cathodes, prepared as described in Example 4.

The devices of the invention may be prepared by any suitable method, but are preferably prepared by depositing relatively thin films of organic and inorganic materials onto a transparent substrate, starting with an anode material, optionally followed by one or more films of any additional organic or inorganic hole-transport materials, followed by one or more films of at least one electroluminescent polymer, optionally followed by any additional layers of organic or inorganic and electron-transport material(s) (in addition to the cathode material), which are then followed by depositing a layer of a cathode material. The layers of material may be prepared by any method suitable for the preparation of a thin film thereof, such as, for example, sputtering, spin-coating, or vapor deposition. Further, the particular technique employed to deposit a thin layer of organic material may require the use of a suitable organic solvent.

The term "anode material" as used herein refers to a semi-transparent or transparent conducting film with a work function between 4.5 eV and 5.5 eV. Examples of suitable anode materials include oxides and mixed oxides of indium and tin, and gold, but is preferably a mixed oxide of tin and indium ("ITO"). The metal oxide is deposited on a transparent substrate such as glass or a solvent-resistant transparent plastic material such as a polycarbonate sheet, so that the light emitted by the electroluminescent organic film may be observed.

The organic film(s) within the device may be a multi-layer composite of several individual layers, each of which are designed for a distinct function, or may be one or more layers of a single material. Since holes are injected from the anode material, any organic film next to the anode material needs to have the functionality of transporting holes. Similarly, any layer next to the cathode material needs to have the functionality of transporting electrons. A layer of an electroluminescent organic material is also required. In some instances, a single organic material can perform the combined functions of hole and electron transport and light emission. The term "electroluminescent organic film" as used

herein refers to an organic film which, upon the injection of electrons and holes into it from opposite sides of the film, produce excitons which can relax to the ground state by emitting photons, preferably corresponding to wavelengths in the visible range. The term "organic film" as used herein means a film of an organic polymer, or a film of one or more organic molecules deposited by thermal evaporation or by solution processing. It is preferred that the total thickness of each organic film be less than 5000 nanometers (nm). It is more preferred that the thickness of the combined layers of organic film(s) be less than 5000 nm, and most preferably less than 3000 nm.

The ITO-coated glass which preferably serves as the anode and the substrate for depositing the organic film(s) thereon is preferably cleaned with detergent, organic solvents or UV-ozone treatment prior to deposition of the organic film(s). It may also be coated with a thin layer of a conducting substance to facilitate hole transport and/or injection into the electroluminescent film. Such substances include copper phthalocyanine, polyaniline and poly(3,4-ethylenedioxythiophene) (PEDT); the last two in their conductive forms by doping with a strong organic acid such as, for example, poly(styrenesulfonic acid). It is preferred that the thickness of this layer be 200 nm or less; it is more preferred that the thickness be 100 nm or less.

The term "hole-transporting organic film" as used herein refers to a layer of a film of a compound or polymer which, when disposed between two electrodes to which a field is applied and holes are injected from the anode, permits adequate transport of holes into the electroluminescent organic film. The term "electron-transporting organic film" as used herein refers to a layer of a film of a compound or polymer which, when disposed between two electrodes to which a field is applied and electrons are injected from the cathode, permits adequate transport of electrons into the electroluminescent organic film. If a separate hole-transport organic film and/or electron-transport film is used to prepare the electroluminescent device, such films may also have some degree of electroluminescence, but their electroluminescence efficiency will be less than that of the electroluminescent film.

Hole-transporting polymers typically are comprised of triarylamine moieties. In cases where a separate organic layer selected for its hole-transport properties is utilized, the polymeric arylamines described in U.S. Patent application Serial No. 08/606,180, filed on February 23, 1996; U.S. Patent application Serial No. 08/696,280, filed on August 13, 1996; U.S. Patent application Serial No. 08/967,347, filed on October 27, 1997; and U.S. Patent

5,728,801. Other known hole-conducting polymers, such as polyvinylcarbazole, may also be used.

Alternatively, the hole-transporting polymer for these devices may be selected from among semi-conducting polymers such as doped polyaniline, doped poly(3,4-ethylene-dioxythiophene), and doped polypyrrole. By "doping" is meant the blending of a semiconducting polymer (such as emeraldine base of polyaniline and poly(3,4-ethylene-dioxythiophene)) with an additive which renders the resulting polymer compositions more conductive. Preferably, the conducting polymer is derived from blending poly(3,4-ethylene-dioxythiophene) with a polymeric acid. More preferably, the polymeric acid contains sulfonic acid groups, and is most preferably poly(styrenesulfonic acid). Most preferred are polymer compositions derived from blending poly(3,4-ethylenedioxythiophene) with at least two equivalents of poly(styrenesulfonic acid).

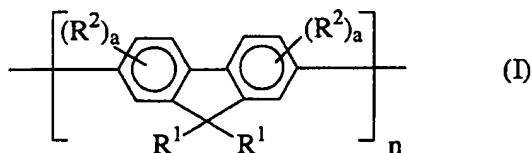
The resistance of this hole-transport layer to erosion by the solution of the organic films which may be subsequently applied to the composite structure is obviously critical to the successful fabrication of multi-layer devices. Resistance to erosion may be increased by, for example, choosing a high molecular weight or crosslinkable hole-transport polymer, or by selecting a hole-transport polymer which is insoluble in the particular solvent used to deposit the electroluminescent polymer. The thickness of this hole-transport layer is preferably 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less. In a preferred embodiment, layers of hole-transporting polymer films are arranged so that the layer closest to the anode has the lower oxidation potential, with the adjacent layers having progressively higher oxidation potentials. By these methods, electroluminescent devices having relatively high light output per unit voltage may be prepared.

In the case where a separate electron-transporting organic layer is used, it may be applied either by thermal evaporation of low molecular weight materials or by solution coating of a polymer with a solvent that would not cause significant damage to the underlying electroluminescent organic film. Examples of low molecular weight materials include the metal complexes of 8-hydroxyquinoline (as described in Burrows et al., Applied Physics Letters, Vol. 64, pp. 2718-2720 (1994)), metallic complexes of 10-hydroxybenzo(h)quinoline (as described in Hammed et al., Chemistry Letters, pp. 906-906 (1993)), 1,3,4-oxadiazoles (as described in Hammed et al., Optoelectronics - Devices and Technologies, Vol. 7, pp. 83-93 (1992)), 1,3,4-triazoles (as described in Kido et al.,

Chemistry Letters, pp. 47-48 (1996)), and dicarboximides of perylene (as described in Yoshida et al., Applied Physics Letters, Vol. 69, pp. 734-736 (1996)).

Polymeric electron-transporting materials useful in making electron-transporting organic films are exemplified by 1,3,4-oxadiazole-containing polymers (as described in Li et al., Journal of Chemical Society, pp. 2211-2212 (1995), and in Yang and Pei, Journal of Applied Physics, Vol. 77, pp. 4807-4809 (1995)), 1,3,4-triazole-containing polymers (as described in Strukelj et al., Science, Vol. 267, pp. 1969-1972 (1995)), quinoxaline-containing polymers (as described in Yamamoto et al., Japan Journal of Applied Physics, Vol. 33, pp. L250-L253 (1994), and in O'Brien et al., Synthetic Metals, Vol. 76, pp. 105-108 (1996)), cyano-PPV (as described in Weaver et al., Thin Solid Films, Vol. 273, pp. 39-47 (1996)), and fluorene-containing polymers, as described, for example, in U.S. Patent 5,708,130 and in U.S. Patent application Serial No. 08/861,469, filed on May 21, 1997. The thickness of this layer may be 500 nm or less, preferably 300 nm or less, most preferably 150 nm or less.

In a preferred embodiment, the electroluminescent organic film is a film containing a polyfluorene, and preferably comprises at least fifty percent by weight of a polyfluorene of the formula:



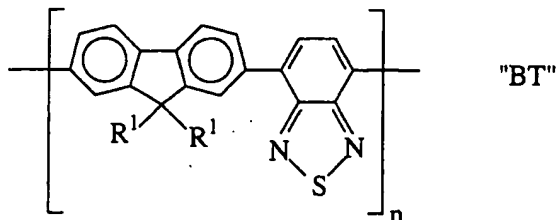
wherein R^1 is independently in each occurrence H , C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing one or more S , N , O , P or Si atoms, C_{4-16} hydrocarbyl carbonyloxy, C_{4-16} aryl(trialkylsiloxy) or both R^1 may form with the 9-carbon on the fluorene ring a C_{5-20} cycloaliphatic structure or a C_{4-20} cycloaliphatic structure containing one or more heteroatoms of S , N or O ;

R^2 is independently in each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

a is independently in each occurrence a number of from 0 to 3; and

n is a number greater than 10.

In the above formula, R¹ is preferably in each occurrence n-octyl. More preferably, the electroluminescent organic film additionally comprises from 0.1 to 50 percent by weight of a polymer of the formula:



5 The BT polymer is preferably used in an amount, based on the weight of the polymers in the blend, of at least 1 percent, more preferably at least about 3 percent; but preferably no greater than 20 percent, more preferably no greater than 10 percent, and most preferably no greater than 5 percent.

10 The term "cathode material" as used herein refers to a conducting metal film with a work function between 2.5 eV and 4.5 eV. In the device of the first aspect of the invention, the cathode material comprises ytterbium. The cathode of ytterbium may be deposited by any suitable technique, such as thermal evaporation or by sputtering. The thickness of the cathode is preferably from 100 nm to 10,000 nm. If desired, the film of ytterbium may be coated with another film of a metal having a higher work function, such as
15 aluminum or silver, to improve stability. The thickness of the additional layer is preferably at least 100 nm, more preferably at least 250 nm, most preferably at least 500 nm; but preferably no greater than 10,000 nm, more preferably no greater than 5,000 nm, and most preferably no greater than 1,000 nm. Among all metals which form the organic/metal interface between the organic material(s) and the metal cathode, ytterbium preferably
20 comprises at least 20 percent of the thickness of such film, more preferably at least 50 percent, and most preferably 100 percent.

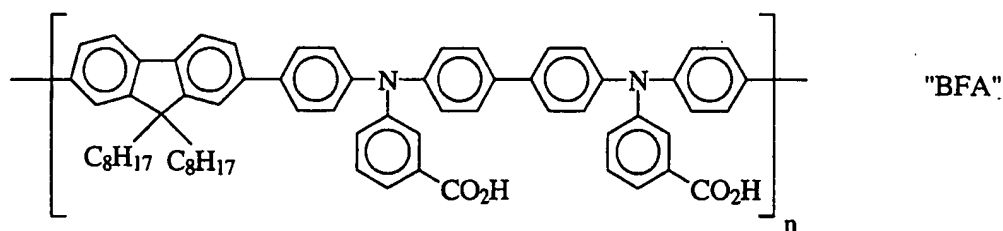
 In the second aspect of the invention, the cathode is prepared by evaporating and vapor depositing magnesium and at least one metal having a higher work function than magnesium, wherein the source of metal used for the process is an alloy of
25 such metals. Surprisingly, it has been discovered that evaporation of an alloy results in the formation of relatively smooth and uniform layer(s) of metal of the cathode which adhere well to the substrate on which they are deposited, even though the metals present in the alloy may evaporate at different rates and temperatures. The metal which has a higher work

function than magnesium (as described in Sze, S., Physics of Semiconductor Devices, John Wiley and Sons, 1981, p. 251) is preferably aluminum. The composition of the alloy is preferably at least 85 weight percent magnesium, more preferably at least 90 weight percent, most preferably at least 93 weight percent; but preferably no greater than 98 weight percent, more preferably no greater than 96 weight percent, and most preferably no greater than 95 weight percent. Most preferably, the alloy is Dowmetal (92.7 percent magnesium, 6 percent aluminum, 1 percent zinc, and 0.3 percent manganese).

The devices of this invention preferably emit light having a brightness of at least 1000 Cd/m² when subjected to an applied voltage of no more than 50 volts, preferably no more than 10 volts, and most preferably no more than 5 volts. Their luminance efficiency may be as high as 3.5 Cd/A or higher. Their resistance to environmental degradation may be measured by testing their luminance efficiency (Cd/A) at a voltage of 9 volts, exposing the devices to ambient conditions (23°C, 25 percent relative humidity) for 22 days, and then re-testing their luminance efficiency and light output at the same voltage. Their luminance efficiencies and light output preferably do not decrease by more than 40 percent, and more preferably by no more than 15 percent.

Example 1

ITO-glass was cleaned by sonication with toluene, detergent, deionized water, and ethanol, and finally treated with UV-ozone. A film (about 40 nm) of a polymer having the formula:



was deposited by spin-coating from an N,N-dimethylformamide solution. The film was dried in vacuum at 60°C for several hours. A film of a 95/5 F8-BT blend (about 100 nm film thickness) was deposited onto the BFA film by spin-coating from a xylene solution, followed by solvent removal in vacuum at room temperature for several hours. Because BFA is completely insoluble in xylene, its film does not suffer any erosion during the deposition of the second polymer film. A set of devices were prepared with calcium cathodes (as a

comparative example and not as an example of the invention) and another set with ytterbium cathodes, by thermal evaporation at about 10^{-6} Torr. The devices were tested in a glove box at a positive bias (ITO as the anode) and brightness and current density as a function of bias voltage were recorded. Device brightness was measured in candelas per square meter (Cd/m²), and efficiency was measured in candelas per ampere (Cd/A). A comparison of brightness between an ytterbium and calcium device (Figures 1 and 2) showed that an ytterbium cathode produces a device with a higher luminance and efficiency over the entire range of bias voltage.

To test the stability of the Yb cathode devices at ambient conditions, two sets of ytterbium-cathode devices were removed from the glove box and left in room air (relative humidity between 20 to 50 percent and a temperature of about 23°C). One set was tested after 4 days of exposure to room air and the second set tested after 22 days of exposure. Device efficiencies at 1500 Cd/m² are calculated and given in Table I. As can be seen from the data, device efficiency was unaffected after 4 days of exposure to room air. Even after 22 days, the devices still retained more than 50 percent of their original efficiency.

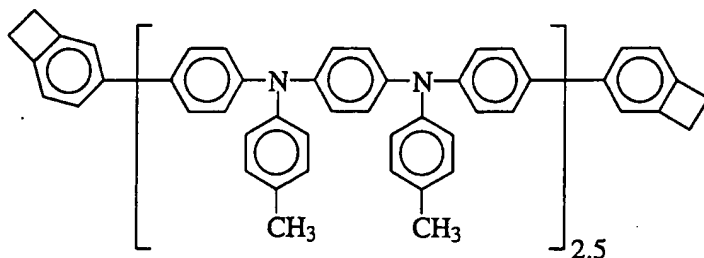
Table I. Device Stability.

| Example | Exposure (Days) | Efficiency at 1500 Cd/m ² (Cd/A) | |
|---------|--------------------|---|----------------|
| | | As Prepared | After Exposure |
| 1a | 4 | 4.17 | 4.05 |
| 1b | 4 | 3.85 | 4.05 |
| 1c | 4 | 3.06 | 3.41 |
| 1d | 22 | 4.59 | 3.70 |
| 1e | 22 | 4.10 | 2.38 |
| 1f | 22 | 3.37 | 2.94 |

Figure 1 is a plot of luminance (Cd/m²: y-axis) versus voltage. Figure 2 is a plot of luminance efficiency (Cd/Amperes: y-axis) versus voltage. The dotted line indicates the data for the calcium cathode device and the solid line indicates the data for the ytterbium cathode device in both figures.

Example 2 - Metallic films on thermosetting polyarylamine (TPA)

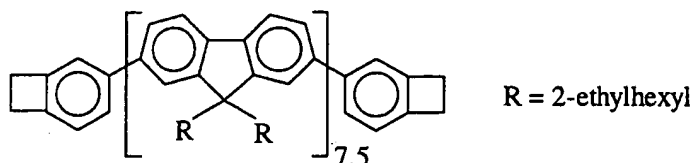
A film of the resin of the formula:



was formed by spin-coating on a polished silicon wafer and was subsequently crosslinked by heating at 250°C for 1 hour. This resin may be prepared as described in PCT Publication No. 97/33193. Following the procedure of Example 1, magnesium film (as a comparative example and not as an example of this invention) and Dowmetal alloy film were deposited on separate coated wafers and were examined by electron microscopy. The large open floret grain structure of the magnesium film and the much finer interlocking grain structure of the Dowmetal alloy film is demonstrated by micrograph analysis.

Example 3 - Metallic films on thermosetting polyfluorene

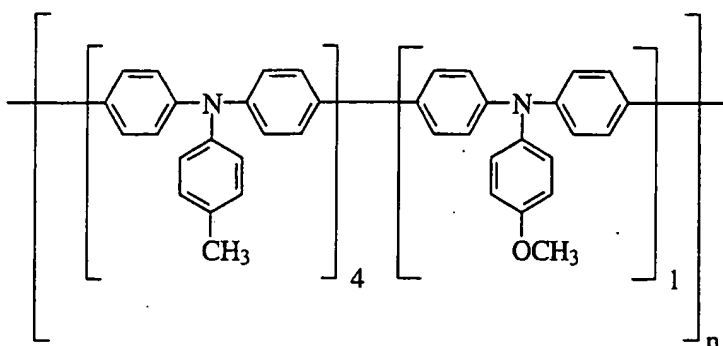
A film of the resin of the formula:



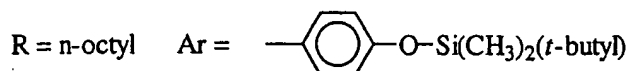
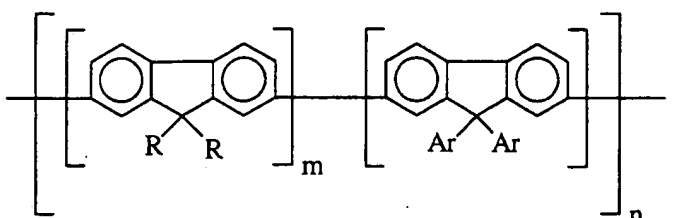
was formed by spin-coating on a polished silicon wafer and was subsequently crosslinked by heating at 250°C for 1 hour. This resin may be prepared as described in U.S. Patent 5,708,130. Following the procedure of Example 1, Dowmetal alloy film was deposited on a coated wafer and examined by electron microscopy. The fine interlocking grain structure of the Dowmetal alloy film was vividly observable by micrograph analysis.

Example 4 - Metallic films on polyarylamine

EL devices were constructed by first depositing onto an indium-tin-oxide coating glass a film of a polyarylamine hole-transporting polymer (structure shown below, wherein n is about 3) by spin-coating from chlorobenzene solution.



A film of an electroluminescent polyfluorene of the following structure:



m is about 10

n is about 3

- 5 prepared as described in Example 16 of U.S. Patent 5,708,130, was then spin-coated from a toluene solution on top of the hole-transporting polyarylamine to give a two-layer structure. Magnesium (as a comparative example and not as an example of the invention) or Dowmetal alloy was then deposited on top of the polymer film by vapor deposition, forming the cathode and completing the EL devices. Blue light was observed from the devices upon
- 10 applying a DC current. It could be seen from the light output (luminous flux) vs. current density plot shown in Figure 3 that the device with Dowmetal alloy as the cathode had significantly higher light output at a given current density. In the typical operating range of 10 to 20 mA/cm², the light output of the Dowmetal alloy device was at least twice as high as that from the device with magnesium cathode. A similar trend was observed by plotting light
- 15 output vs. voltage as shown in Figure 4. The onset of light emission from the device based on Dowmetal alloy was about 10 V or less, significantly lower than that of the magnesium-based device. The improved operating efficiency can be attributed to the more intimate contact and more complete coverage of the polymer film when Dowmetal alloy was used.

The hole-transporting polymer was prepared using the following procedure of copolymerization of N,N-di-(4-bromophenyl)-*p*-tolylamine and N,N-di-(4-bromophenyl)-*p*-anisidine: To a dry reactor equipped with a mechanical stirrer, nitrogen/vacuum inlet, and a rubber septum was added N,N-di-(4-bromophenyl)-*p*-tolylamine (10.0 g, 24 mmol), N,N-di-(4-bromophenyl)-*p*-anisidine (2.6 g, 6 mmol), triphenylphosphine (3.9 g, 15 mmol), zinc powder (5.9 g, 90 mmol) and nickel chloride-2,2'-bipyridine complex (NiCl₂-Bipy) (0.26 g, 0.9 mmol). The reactor was evacuated to about 0.2 mm Hg then purged with nitrogen, this cycle was repeated 7 times. To the reactor was added (via syringe) 50 mL of anhydrous DMAc. The reaction mixture as heated to 80°C with a stirring rate of 250 rpm. After a few minutes the reaction mixture turned from gray to a brownish red color which becomes darker with time. The reaction is stirred at 80°C for 31 hours. The reaction mixture is slowly added to 250 mL of acetone to afford a precipitate. The grayish yellow precipitated is collected and dried. The powdered solid is slowly added to 300 mL of 3N HCl solution with stirring. The mixture is stirred for about 30 minutes where the gray color zinc was digested by the acid leaving a pale yellow precipitate. The yellow precipitate was collected and washed with water (2 x 150 mL), ethanol (2 x 150 mL), and acetone (2 x 150 mL). The solid dissolved in 400 mL of chlorobenzene was added to 250 mL of aqueous 3N HCl. The mixture was stirred at 60°C for 30 minutes. The aqueous layer was removed and the organic layer was washed with water (2 x 250 mL). The chlorobenzene solution was added to a flask containing 100 mL of water and 50 mL of ethylenediamine. The mixture was stirred at 60°C for 2 hours. The aqueous layer was removed and the organic layer was washed with water (3 x 250 mL). The chlorobenzene solution was dried over anhy. MgSO₄, then concentrated under reduced pressure to about 1/5 of the original volume. Product was precipitated from 95 percent ethanol. The yellow precipitate was collected then dried in a vacuum oven overnight to afford a mass of 4.3 g (55 percent, low yield was due to spillage of the chlorobenzene solution). The copolymer was soluble in chlorobenzene and chloroform and slightly soluble in THF, methylenchloride, and toluene. Integration from 1H NMR spectrum of the methyl of the tolylamine vs. the methoxy of the anisidine indicated that the copoly had the desired 4:1 ratio. Cyclic voltammogram of the product in solution (0.2 M tetrabutylammonium perchlorate in dichloromethane, referenced to Ag/AgCl electrode) indicated a E1ox = +0.58V and E2ox = +0.88V. While a film coated on platinum electrode revealed Eox = +0.82V (rev).

DSC analysis of the product revealed a glass transition point of 234°C. GPC analysis of the copolymers indicated an Mn = 4600 with a polydispersity of 2.01. The inherent viscosity (η_{inh}) was determined to be 0.15 dL/g (0.5g/dL in chlorobenzene at 25°C). Elemental analysis of the copolymer by X-ray fluorescence revealed no detectable amount of nickel, zinc, or copper. The

material in the solid state had a strong UV absorption (λ_{max} 374 nm) and a solution (THF) absorption of 372 nm. The material in the solid state had a photoluminescent peak at 428 nm and a solution (THF) emission at 421 nm.

Figure 3 is a plot of luminous flux (mLumens; y-axis) versus mA/cm². Figure 4
5 is a plot of luminous flux (mLumens; y-axis) versus volts. The solid markings indicate the data for the Dowmetal cathode device and the open markings indicate the data for the magnesium cathode device in both figures.

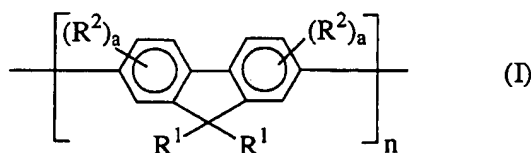
CLAIMS:

1. An electroluminescent device comprising at least one organic film, at least one of which is an electroluminescent organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes and electrons are injected into the electroluminescent organic film, resulting in light emission therefrom;

wherein the cathode material comprises a film of ytterbium.

2. The device of claim 1 wherein the electroluminescent organic film is a film containing a polyfluorene.

3. The device of Claim 1 wherein the electroluminescent organic film comprises at least fifty percent by weight of a polymer of the formula:

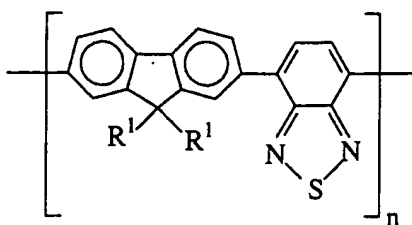


- wherein R^1 is independently in each occurrence H, C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing one or more S, N, O, P or Si atoms, C_{4-18} hydrocarbyl carbonyloxy, C_{4-18} aryl(trialkylsiloxy) or both R^1 may form with the 9-carbon on the fluorene ring a C_{5-20} cycloaliphatic structure or a C_{4-20} cycloaliphatic structure containing one or more heteroatoms of S, N or O;

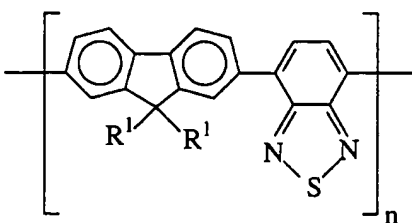
R^2 is independently in each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thiopether, C_{1-20} hydrocarbylcarbonyloxy or cyano;

- a is independently in each occurrence a number of from 0 to 3; and n is a number greater than 10.

4. The device of claim 3 wherein a is 0 and each R^1 is n-octyl.
5. The device of claim 2 wherein the electroluminescent organic film additionally comprises at least 1 percent by weight of a polymer of the formula:

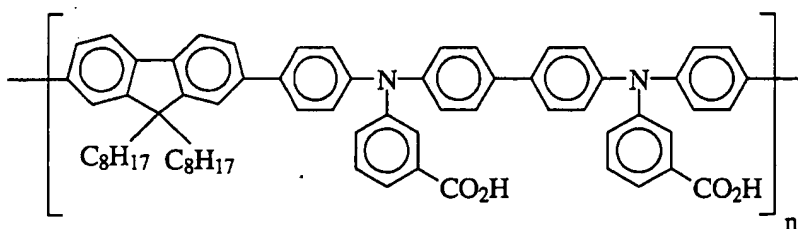


6. The device of Claim 4 wherein the electroluminescent organic film consists of 90 to 98 percent by weight of the polymer of Formula (I) and 2 to 10 percent by weight of a polymer of the formula:



5

7. The device of Claim 2 which additionally contains an organic film positioned between the electroluminescent organic film and the anode, the film comprising a polymer of the formula:



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8. The device of claim 1 wherein the electroluminescent organic film is in direct contact with a hole-transporting organic film, which is positioned between the electroluminescent polymer film and a film of indium-tin oxide or a second hole-transporting organic film.

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9. The device of Claim 1 wherein the film of ytterbium is in direct contact with the electroluminescent organic film.

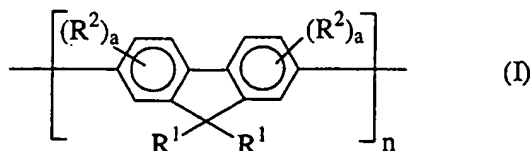
10. The device of Claim 4 wherein the device additionally comprises a layer of an electron-transporting organic film in contact with the film of ytterbium, and positioned between the film of ytterbium and the electroluminescent organic film.

11. An electroluminescent device comprising at least one organic film, at least one of which is an electroluminescent organic film, arranged between an anode material and a cathode material such that under an applied voltage, the device is forward biased and holes and electrons are injected into the electroluminescent organic film,
 5 resulting in light emission therefrom;

wherein the cathode material comprises a metal film prepared by vapor deposition or sputtering of an alloy of magnesium and a second metal having a higher work function, such alloy having a magnesium content of from 80 to 98 percent.

12. The device of Claim 11 wherein the electroluminescent organic film is a
 10 film containing a polyfluorene.

13. The device of Claim 11 wherein the electroluminescent organic film comprises at least fifty percent by weight of a polymer of the formula:

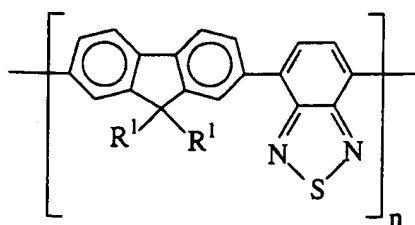


- wherein R^1 is independently in each occurrence H, C_{1-20} hydrocarbyl or C_{1-20} hydrocarbyl containing one or more S, N, O, P or Si atoms, C_{4-16} hydrocarbyl carbonyloxy, C_{4-16} aryl(trialkylsiloxy) or both R^1 may form with the 9-carbon on the fluorene ring a C_{5-20} cycloaliphatic structure or a C_{4-20} cycloaliphatic structure containing one or more heteroatoms of S, N or O;

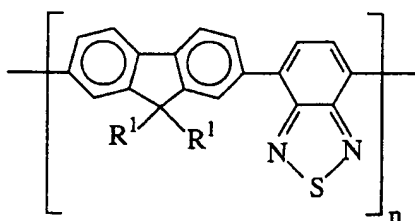
- R^2 is independently in each occurrence C_{1-20} hydrocarbyl, C_{1-20} hydrocarbyloxy, C_{1-20} thioether, C_{1-20} hydrocarbyl carbonyloxy or cyano;

a is independently in each occurrence a number of from 0 to 3; and n is a number greater than 10.

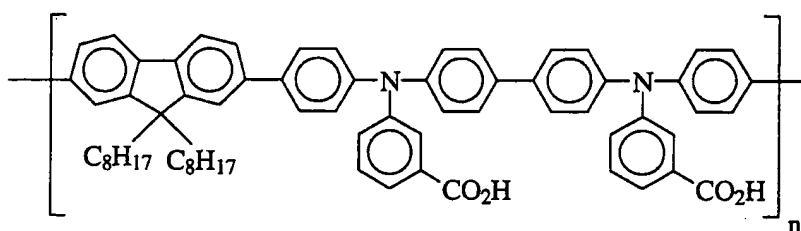
14. The device of claim 13 wherein a is 0 and each R^1 is n -octyl.
15. The device of claim 11 wherein the electroluminescent organic film
 25 additionally comprises at least 1 percent by weight of a polymer of the formula:



16. The device of Claim 11 wherein the electroluminescent organic film consists of 90 to 98 percent by weight of a polymer of Formula (I) and 2 to 10 percent by weight of a polymer of the formula:



17. The device of Claim 11 which additionally contains an organic film positioned between the electroluminescent organic film and the anode, the film comprising a polymer of the formula:



18. The device of Claim 11 wherein the electroluminescent organic film in direct contact with a hole-transporting organic film, which is positioned between the electroluminescent polymer film and a film of indium-tin oxide or a second hole-transporting organic film.

19. The device of Claim 11 wherein the film of the alloy is in direct contact with the electroluminescent organic film.

20. The device of Claim 11 wherein the device additionally comprises a layer of an electron-transporting organic film in contact with the film of the alloy, and positioned between the film of the alloy and the electroluminescent organic film.

21. The device of Claim 11 wherein the metal film is prepared by vapor deposition of the alloy.

Figure 1. Luminance Comparison: Yb vs Ca Cathodes

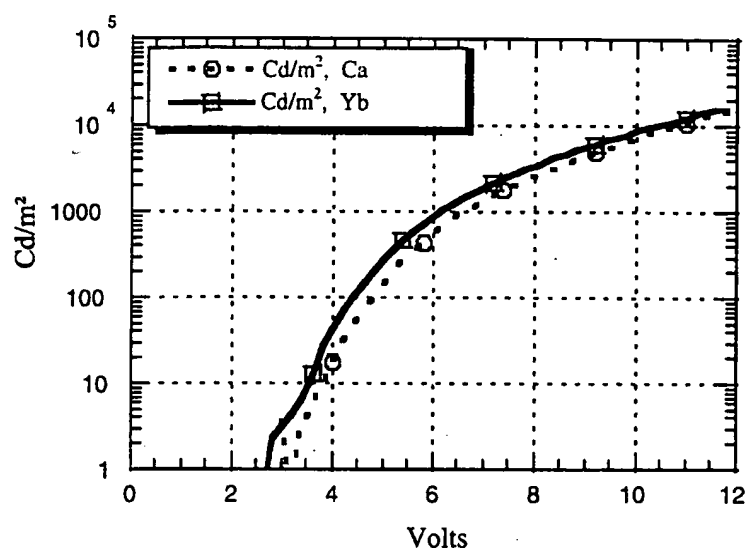


Figure 2. Efficiency Comparison

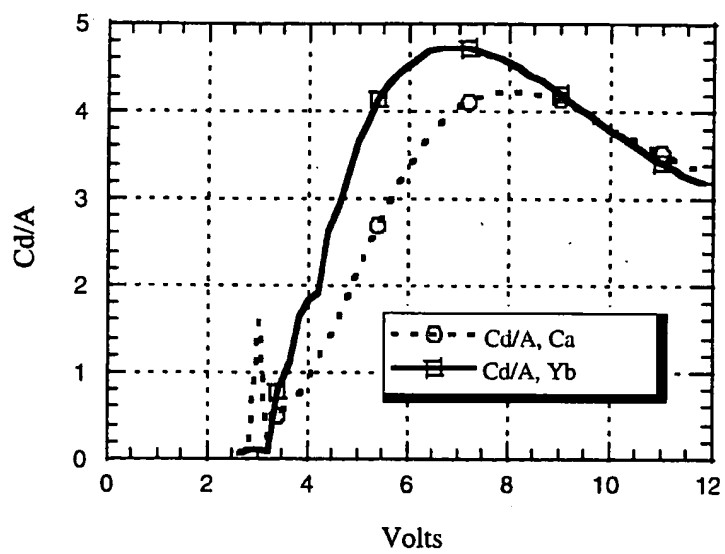


Figure 3. Mg vs. DM comparison

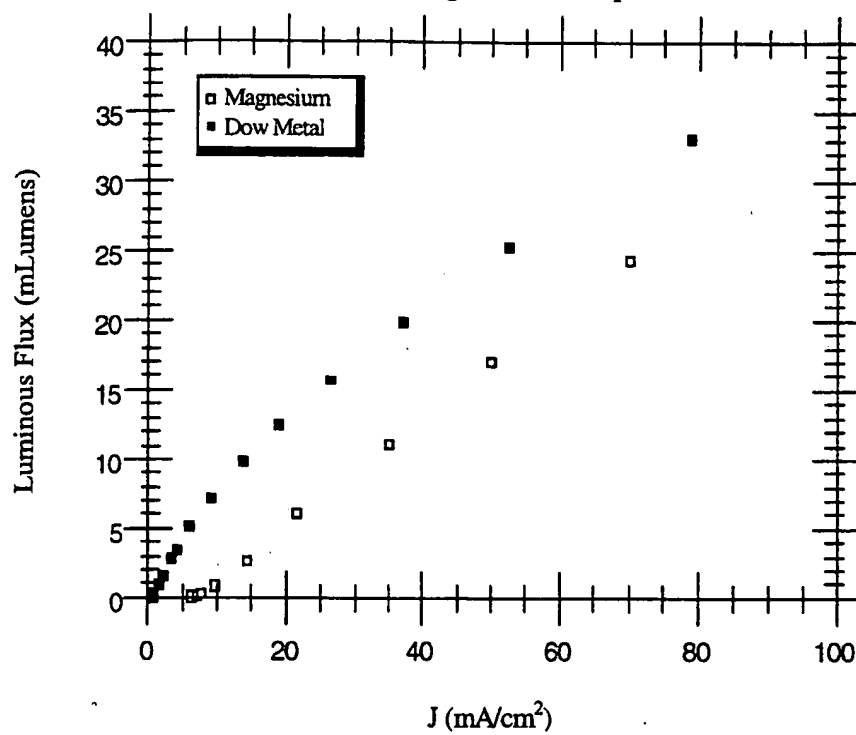
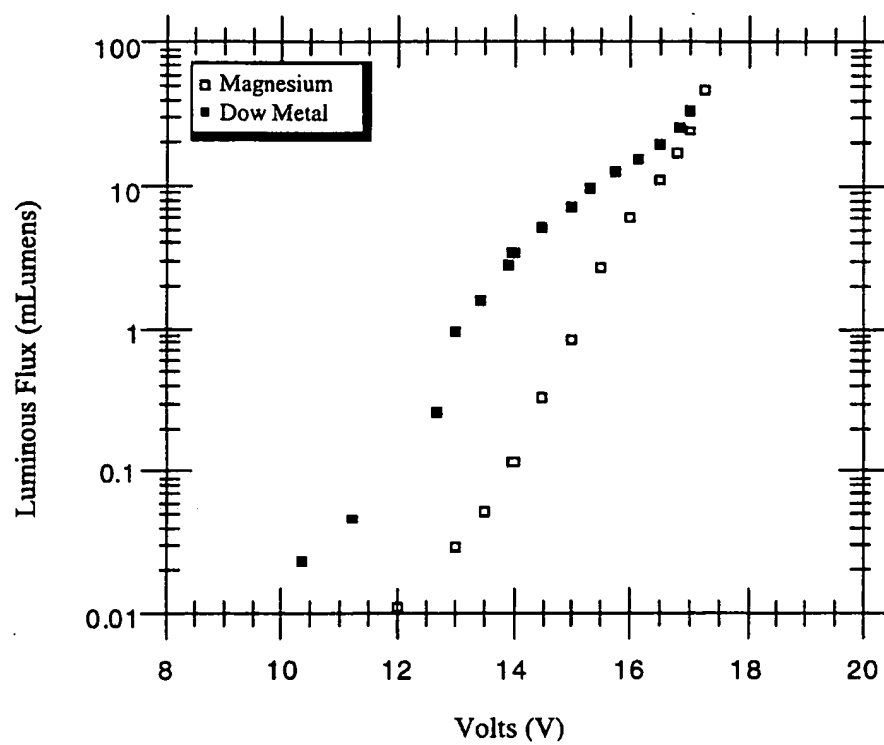


Figure 4. Mg vs. DM comparison



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/06291

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01L51/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01L H05B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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| X | HIROYUKI SUZUKI ET AL: "ORGANIC LIGHT-EMITTING DIODES WITH RADIO FREQUENCY SPUTTER- DEPOSITED ELECTRON INJECTING ELECTRODES" APPLIED PHYSICS LETTERS, vol. 68, no. 16, 15 April 1996 (1996-04-15), pages 2276-2278, XP000585170 ISSN: 0003-6951 the whole document | 11 |

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Date of the actual completion of the international search

16 July 1999

Date of mailing of the international search report

23/07/1999

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De Laere, A

INTERNATIONAL SEARCH REPORT

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Information on patent family members

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PCT/US 99/06291

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
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